5.5.2. TRANS-SIBERIAN OBSERVATIONS INTO THE CHEMISTRY OF THE ATMOSPHERE (TROICA)

From June 27 to July 10, 2001, about 11,000 in situ measurements of CFC-12, halon-1211, N_2O, and SF_6, and nearly 5000 measurements of CFC-11, CFC-113, $CHCl_3$, CH_3CCl_3, CCl_4, CH_4, and H_2 were made along 17,000 km of the fully electrified trans-Siberian railway between Moscow and Khabarovsk, Russia (Figure 5.38), with the ACATS-IV gas chromatograph (GC). These measurements were part of the seventh Trans-Siberian Observations into the Chemistry of the Atmosphere (TROICA-7) scientific expedition, a collaboration between CMDL, the Coooperative Institute for Research in Environmental Sciences (CIRES), NASA, the Max Planck Institute for Chemistry (Mainz, Germany), and the Russian Institute of Atmospheric Physics (Moscow). TROICA expeditions were inaugurated by German and Russian scientists in 1995 and have taken place annually during different seasons [*Crutzen et al.*, 1998; *Oberlander et al.,* 2002]. The primary CMDL objective for TROICA-7 was to make frequent (every 70 or 140 seconds) measurements of halocarbon and greenhouse gases along the trans-Siberian railway, creating a database to which future TROICA measurements of these gases can be compared. CMDL participation in TROICA-7 produced the first extensive set of halocarbon measurements in Russia by American scientists.

Fig. 5.38. Route of the TROICA-7 science expedition along the trans-Siberian railway. Each of the transects, Moscow-Khabarovsk and Khabarovsk-Moscow, was approximately 8500 km in length and took 6.25 days. Major cities along the railway are indicated by filled circles.

As during past TROICA expeditions, German and Russian scientists operated in situ analyzers for CO, CO_2, O_3, CH_4, NO_x, ^{222}Rn, H_2O, aerosols, solar radiation, temperature, pressure, and relative humidity [*Crutzen et al.*, 1998]. A global positioning system receiver tracked movements of the train, and visual observations along the route were recorded in detail. A microwave temperature profiler was also part of the payload. All instruments were housed in a special rail car (Research Institute of Railroad Transport of Russia) situated immediately behind the electric locomotive. Air intakes for instruments were attached to a frame structure on top of the science car. ACATS-IV sampled air at approximately 4 L min^{-1} through 5 m of 6.4-mm-outside-diameter Dekabon tubing with a Teflon diaphragm pump (model UN05, KNF Neuberger Inc., Princeton, New Jersey). A 2-mm-pore glass fiber filter was used to keep large particles out of the intake tubing. The sample stream was dried with $Mg(ClO_4)_2$.

The train traveled at a mean and maximum speed of 57 and 129 km h^{-1}. Numerous stops were made during the 6.25 days required to travel each direction. There were 216 scheduled stops at stations with durations of 2-90 minutes. Track maintenance and stop signals accounted for 43 unscheduled, non-station stops with durations of 1-69 minutes. In general, population density decreased with distance from Moscow, though large, industrialized cities were encountered almost daily along the length of the railway. East of the Ural Mountains, the population density is greatest in southern Siberia, near the railway. Rural areas were typically birch and larch forest (taiga) or rolling grasslands with some large lowland areas. The Moscow-Khabarovsk segment of the railway spans latitudes of 48.6° to 58.6°N and altitudes of 0 to 998 m above sea level. Temperature ranged from 3° to 33°C, with three daytime highs >30°C and three nighttime lows <10°C. Rain, heavy at times, was encountered on 12 of the 14 travel days.

Large fluctuations in the mixing ratios of some gases were observed during the expedition, as illustrated by the time series for the refrigerant CFC-12 and fire extinguishing agent halon-1211 (Figure 5.39). The variability (1 standard deviation) of every gas measured along the railway was at least 50% greater than its measurement precision (Table 5.8). Variability relative to the mean mixing ratio was very high (>70%) for $CHCl_3$ and CO; 11-32% for CFC-12, halon-1211, H_2, and CO_2; 6-9% for CFC-113 and CH_4; and <3% for N_2O, SF_6, CFC-11, CH_3CCl_3, and CCl_4. Fluctuations in mixing ratio observed along the railway were also much greater than at Point Barrow, Alaska (BRW), during June-July 2001 (Table 5.8) except for CH_3CCl_3, which showed about the same low variability at both locations. Ratios of TROICA-7 to BRW variability for gases other than CH_3CCl_3 ranged from 1.7 for SF_6 to 59 for CFC-12.

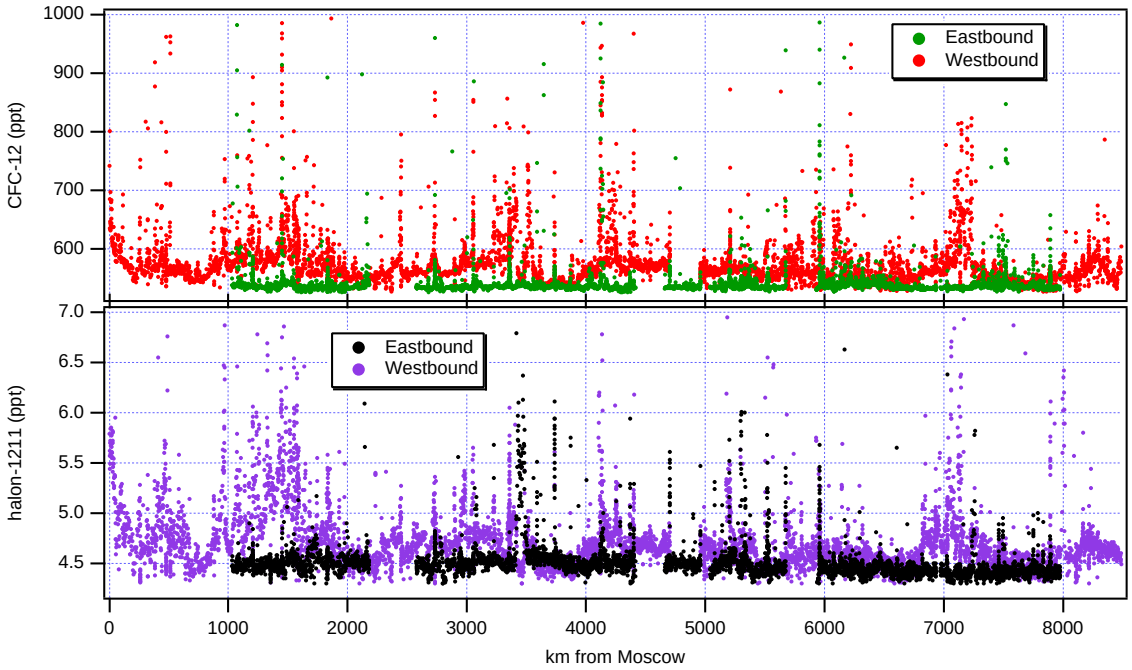

Fig. 5.39. Time series of CFC-12 (top) and halon-1211 (bottom) mixing ratios during TROICA-7 as a function of distance from Moscow. For CFC-12, there were 34 and 83 measurements >1000 ppt during the eastbound and westbound transects, respectively, that are off-scale in this figure. There were 2 eastbound and 41 westbound halon-1211 measurements >7 ppt that are off-scale. Of interest for these two gases are their high variability along the railway and their generally higher mixing ratios during the westbound transect.

TABLE 5.8. Summary Statistics of Gas Measurements During TROICA-7 and at Barrow, Alaska

	TROICA-7							
Gas	N	Mean	Median	Precision*	Variability†	$75^{th} - 25^{th}$ Percentile	$95^{th} - 5^{th}$ Percentile	BRW Variability‡
N_2O (ppt)	10815	316.7	316.4	0.6	1.9	1.1	3.7	0.8
SF_6 (ppt)	11086	5.00	4.99	0.05	0.15	0.07	0.19	0.09
CFC-12 (ppt)	11132	573	551	4	118	36	123	2
Halon-1211 (ppt)	11125	4.66	4.55	0.04	0.52	0.25	0.94	0.04
CFC-11 (ppt)	4629	263.0	262.0	0.5	5.3	1.3	6.3	1.2
CFC-113 (ppt)	4573	82.3	81.9	0.3	7.2	0.9	2.3	0.7
$CHCl_3$ (ppt)	4929	16.3	14.1	0.2	12.6	4.2	15.3	1.7
CH_3CCl_3 (ppt)	4700	38.9	38.8	0.5	0.8	1.1	2.1	0.8
CCl_4 (ppt)	4690	102.7	102.5	0.4	2.5	0.6	2.3	0.4
H_2 (ppb)	4634	549	507	14	177	66	350	15
CO (ppb)	8241	146	126	10	102	59	218	5
CH_4 (ppb)	4459	1882	1852	16	109	83	212	21
CO_2 (ppm)	10706	379.3	365.3	1	41.8	24.9	127.8	1.4

*Precision is expressed as the standard deviation of residuals of ACATS-IV calibration measurements made during the expedition, where residuals are deviations of raw calibration data from smoothed, drift-corrected calibration data.

†TROICA-7 variability is expressed as 1 standard deviation.

‡ BRW variability is expressed as the standard deviation of residuals of hourly averages of in situ observations made at Point Barrow, Alaska (72° N), during June-July 2001. Residuals are deviations from smooth curve fits to the data that account for seasonal cycles and longer-term trends.

For gases that exhibited concentrations higher than the northern hemispheric background, a major concern is the possibility of air sample contamination due to train-based sources forward and/or aft of the sampling inlets. No known sources of the measured gases were located forward of the sample inlets, but >100 m aft there were small coal-fired water heaters in passenger carriages and a working air conditioner in the restaurant car. There was also an inoperative air conditioning unit in the science carriage with no discernible pressure of CFC-12. Intuitively, a forward source would frequently contaminate the air stream sampled by instruments, especially at high train speeds. An aft source could have contaminated samples when the train was moving slowly or stopped.

To explore the possibility of contamination by train-based sources, data for four highly variable gases (CFC-12, halon-1211, CO, and CO_2) were separated by train speed: high, low, and stopped. Forward contamination of samples was investigated by comparison of data at high train speeds with CMDL data at remote, high-latitude northern hemisphere sites during June-July 2001. For these gases, 30-60% of the data taken at high train speeds were representative of well-mixed, background air masses, indicating that samples were not consistently contaminated by forward sources. This is supported by the fact that elevated mixing ratios (>80th percentile) were detected less frequently at high train speeds than when the train was stopped. However, this evidence, along with significantly lower fractions of background CFC-12 and CO mixing ratios at stops compared with high train speeds, suggests that aft sources on the train many have contaminated samples when the train was stopped. Of course, these biases may simply reflect the fact that the train stopped primarily at stations in populated areas where sources were present. To explore train contamination from aft sources during stops, CFC-12, halon-1211, CO, and CO_2 measurements made at scheduled station stops were separated from those made at unscheduled, non-station stops. For these four gases, fractions of background data at non-station stops (57-80%) were 1.4 to 2.3 times greater than at station stops (24-47%). Fractions of elevated mixing ratios at station stops were also factors of 1.3 to 3.5 higher than at non-station stops. Though these statistics for station and non-station stops do not preclude the possibility of sample contamination by the train during stops, they strongly imply that sources proximate to train stations in populated areas were responsible for the elevated mixing ratios measured during stops.

CFC-12 and halon-1211 concentrations were quite variable during both the eastbound and westbound transects of TROICA-7 (Figure 5.39), but were generally higher throughout the westbound return to Moscow because of large, sustained concentration increases observed on some nights. These increases, also seen in CO_2, ^{222}Rn, and $CHCl_3$ data (Figures 5.40 and 5.4**1**), occurred beneath nocturnal temperature inversions that were much stronger and prolonged during the westbound transect (Figures 5.40a and 5.41a). Increases in ^{222}Rn and CO_2 beneath the nighttime inversions were generally broad and well-correlated because both gases are widely emitted by soils. Similar nighttime increases in ^{222}Rn, CO_2, and other gases have been observed during previous TROICA expeditions [*Bergamaschi et al.,* 1998; *Crutzen et al.,* 1998; *Oberlander et al.,* 2002]. $CHCl_3$, CFC-12, and halon-1211 mixing ratios increased broadly beneath several nighttime inversions and sharply near some cities. Nighttime increases in these halocarbons were typically coincident with increased ^{222}Rn and CO_2, but their magnitudes were not generally consistent with ^{222}Rn and CO_2 increases, possibly because of geographical variations in the strengths of halocarbon sources.

Analyses of the TROICA-7 data continue in an effort to characterize the source emissions, transport, and boundary layer dynamics responsible for the observed trace gas variability. Under the *Montreal Protocol on Substances that Deplete the Ozone Layer* [*UNEP*, 1987], non-Article 5 (developed) countries like Russia and the United States were required to cease production of halons and CFCs by January 1994 and 1996, respectively. Economic difficulties prevented Russia from meeting these target dates. Only with substantial financial incentives did Russia finally cease CFC and halon production in December 2000. Inspectors have since verified that Russia is no longer producing CFCs and halons. It is of great interest now to determine whether the detected emissions of CFC-12 and halon-1211 along the trans-Siberian railway are related to stockpile leaks, discharges from in-use structures and equipment, or seepage from abandoned structures and discarded equipment. CMDL scientists intend to be part of the next TROICA expedition proposed for winter 2002/2003.

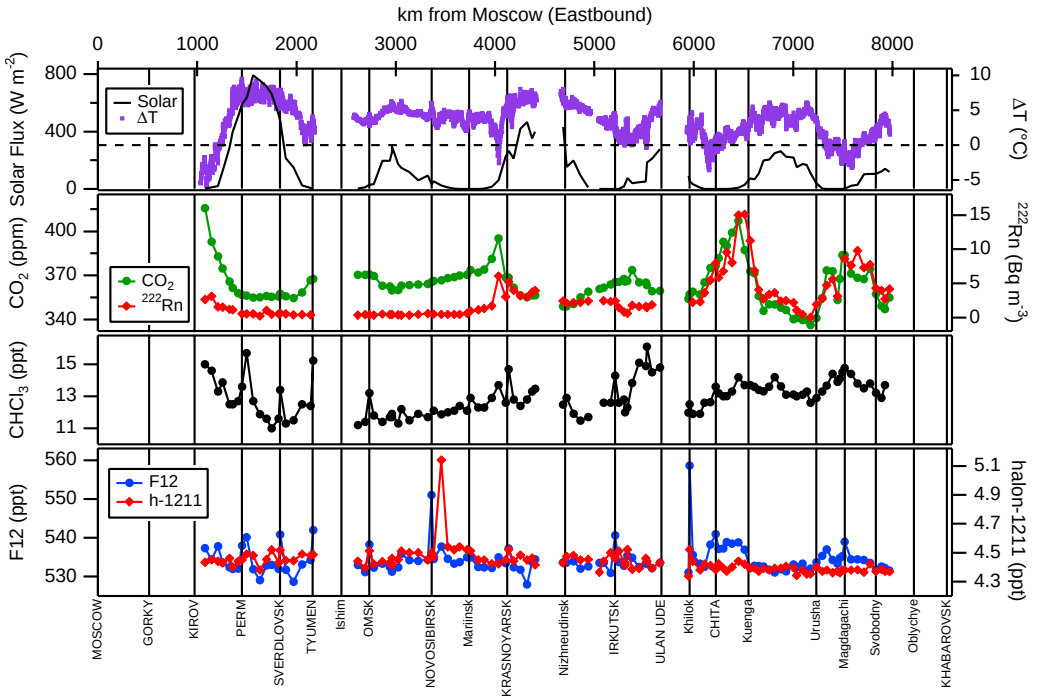

Fig. 5.40. Solar flux, temperature difference, and mixing ratios for CO_2, ^{222}Rn, CFC-12, halon-1211, and $CHCl_3$ during the eastbound transect of TROICA-7. The mixing ratios of these gases increased broadly beneath relatively weak temperature inversions during several nights of the transect. CFC-12, halon-1211, and $CHCl_3$ mixing ratios also sharply increased near several cities. Data for these gases are the 20th percentiles in 1-h windows. Solar fluxes identify daytime and nighttime periods. ΔT is the difference in temperature at 0 and 600 m above the science car roof such that $\Delta T < 0$ indicates a temperature inversion. Major cities along the railway are listed along the bottom axis.

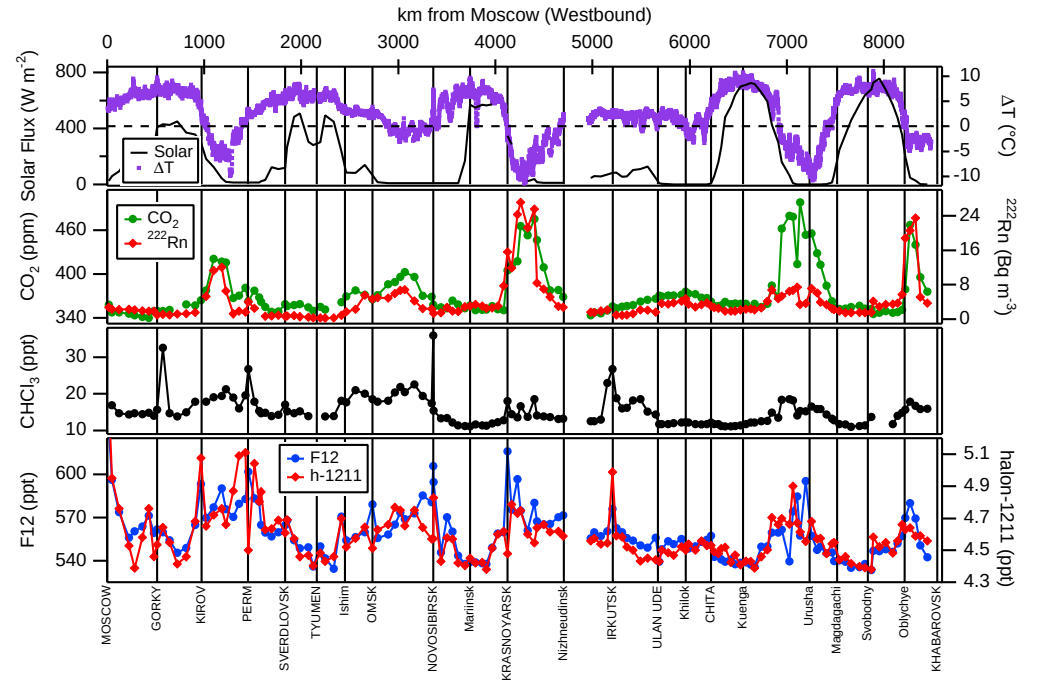

Fig. 5.41. Same as Figure 5.40, except for the westbound transect of TROICA-7. Time series should be viewed from right to left (east to west) as the train returned to Moscow. Several strong nighttime temperature inversions caused large, broad increases in gas concentrations. Note the greatly expanded concentration ranges compared with those in Figure 5.40, the result of stronger temperature inversions and perhaps greater emissions from upwind sources.